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P. 40

FINAL PROJECT REPORT

Project Title: Low Level Measurements of Atmospheric DMS, H_2S, and SO_2 for GTE/CITE-3

Principal Investigator: Eric Saltzman
Co-Principal Investigator: David Cooper

Grant Number: NASA Research Grant NAG-1-918

Grant Period: 11/1/88 - 10/31/91

Grantee Institution: Rosenstiel School of Marine and Atmospheric Sciences
University of Miami
4600 Rickenbacker Causeway
Miami, FL 33149

(NASA-CR-191635) LOW LEVEL MEASUREMENTS OF ATMOSPHERIC DMS, H2S, AND SO2 FOR GTE/CITE-3 Final Report, 1 Nov. 1988 - 31 Oct. 1991 (Miami Univ.) 40 p

N93-18863

Unclas

G3/45 0137103

Project Summary

This project involved the measurement of atmospheric dimethylsulfide (DMS) and hydrogen sulfide (H_2S) as part of the GTE/CITE-3 instrument intercomparison program. The two instruments were adapted for use on the NASA Electra aircraft and participated in all phases of the mission. This included ground-based measurements of NIST-provided standard gases and a series of airborne missions over the Western Atlantic Ocean.

The analytical techniques used during this study were:

1) For Dimethylsulfide: an automated GC/flame photometric detection system with novel thermoelectric inlet and oven systems. An aqueous solution of potassium iodide was used as the oxidant removal agent in the system.

2) For Hydrogen Sulfide: air samples were collected on treated filters aboard the aircraft. Immediately after each flight the filters were extracted and analyzed via fluorescence quenching.

Both of the analytical systems were integrated into the aircraft and deployed successfully. Although there were numerous repairs needed, there was minimal in-flight downtime during the course of the project.

The results from this project include: the data submittal for intercomparison purposes, the preparation of a manuscript detailing the analytical methods used and the field results. A copy of this manuscript is included in this report. A second manuscript synthesizing field data from a number of investigators is currently in preparation. This synthesis paper will focus on diurnal variations in the concentration of atmospheric DMS observed during flights in the Western South Atlantic.

Overall, the project was extremely successful in that all of the major goals were met. Our instruments exceeded expectations in terms of reliability and sensitivity. Furthermore, good agreement was obtained between the various investigators for the gases which we measured and between our calibration and that of NIST.

The publications resulting from this project include:

Cooper, D.J. and E.S. Saltzman. Measurements of atmospheric dimethyl sulfide, hydrogen sulfide and carbon disulfide during GTE/CITE-3. J. Geophys. Res.

Gregory, G.L., L.S. Warren, M.O. Andreae, A.R. Bandy, R.J. Ferek, J.E. Johnson and E. Saltzman. The comparison of instrumentation for tropospheric measurements of dimethyl sulfide: aircraft results for concentrations at the parts-per-trillion level. To be submitted to J. Geophys. Res.

continued

Saltzman, E.S., D.J. Cooper, S.A. Yvon, M.O. Andreae, T.W. Andreae, A.R. Bandy, T.S. Bates, D.D. Davis, R.J. Ferek, J.E. Johnson, M.C. Shipham and D.C. Thornton. Diurnal Variations in Atmospheric Sulfur Gases Over the Western Equatorial Atlantic Ocean. In preparation for J. Geophys. Res.

Saltzman, E.S. and D.J. Cooper. Diurnal variations in atmospheric DMS over the South Atlantic Ocean. EOS Transactions, Am. Geophys. Union, Fall Meeting, 71: 1254.

Cooper, D.J. and E.S. Saltzman. Measurements of DMS, CS_2, and H_2S during GTE/CITE-3. EOS Transactions, Am. Geophys. Union, Fall Meeting, 71:1257.

Measurements of Atmospheric Dimethylsulfide, Hydrogen Sulfide and Carbon Disulfide during GTE/CITE-3

David J. Cooper[+] and Eric S. Saltzman

Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL 33149

[+]Present Address: Woods Hole Oceanographic Institution, Woods Hole, MA 02543

Abstract. Measurements of atmospheric dimethylsulfide (DMS), hydrogen sulfide (H_2S) and carbon disulfide (CS_2) were made over the North Atlantic and South Atlantic Ocean as part of the GTE/CITE-3 project. DMS and CS_2 samples were collected and analyzed using an automated GC/FPD system with a sampling frequency of ten minutes. H_2S samples were collected using silver nitrate impregnated filters and analyzed by fluorescence quenching. The DMS data from both hemispheres have a bimodal distribution. Over the North Atlantic this reflects the difference between marine and continental air masses. Over the South Atlantic it may reflect differences in the sea surface source of DMS, corresponding to different air mass source regions. The median boundary layer H_2S and CS_2 levels were significantly higher in the northern hemisphere than the southern hemisphere, reflecting the higher frequency of samples influenced by pollutant and/or coastal emissions. Composite vertical profiles of DMS and H_2S are similar to each other, and are consistent with a sea surface source. Vertical profiles of CS_2 have maxima in the free troposphere, implicating a continental source. The low levels of H_2S and CS_2 found in the southern hemisphere constrain the role of these compounds in global budgets to significantly less than previously estimated.

INTRODUCTION

The distribution and chemistry of reduced sulfur gases in the atmosphere are of current interest with regard to several important geochemical processes. Much of the acidity in rainfall can be attributed to oxidized sulfur compounds. Quantification of natural background precursors is therefore an essential step in assessing the magnitude of anthropogenic perturbations, and in predicting the effect of pollutant emission controls. It has also been suggested that the atmospheric cycling of biogenic sulfur gases may play a role in the maintenance of the global energy budget by providing the precursors for the formation of sub-micron sulfate aerosols

(Shaw, 1983). Aerosols derived from a marine sulfur source may be the predominant cloud condensation nuclei over the remote oceans, controlling the albedo of marine clouds (Charlson *et al.*, 1987).

The lifetime of biogenic sulfur gases such as dimethylsulfide, hydrogen sulfide and carbon disulfide is on the order of a day in the troposphere. Hence, even low concentrations may indicate a substantial flux. Most environments contain these gases at the low parts-per-trillion (pptv) level (Maroulis and Bandy, 1977; Slatt *et al.*, 1978; Andreae and Raemdonck, 1983; Andreae *et al.*, 1985; Ferek *et al.*, 1986; Berresheim, 1987; Kim and Andreae, 1987; Saltzman and Cooper, 1988). Many of the problems in the atmospheric chemistry of biogenic sulfur gases are best studied in remote regions where the tropospheric oxidant balance is undisturbed by anthropogenic activities. While primarily an intercomparison study, the GTE/CITE-3 expedition consisted of sampling periods over both the polluted North Atlantic Ocean and the relatively unpolluted tropical South Atlantic Ocean. This offered an excellent opportunity to study the contrast between these two environments. The comprehensive support measurements made during these flights facilitated analysis of the sources, sinks and lifetimes of the various sulfur gases in the different regimes studied.

In this report, we describe an automated sampling and analysis system, and present the first airborne DMS and CS_2 measurements made using such a system. The instrument is discussed in detail here, as it has not previously been described. Some of the analytical principles applied may also be of interest in the analysis of a number of sulfur-containing and other organic compounds. Data are also presented for atmospheric H_2S, simultaneously collected using a $AgNO_3$ impregnated filter technique (Natusch *et al.*, 1972; Cooper and Saltzman, 1987; Saltzman and Cooper, 1988).

SAMPLING AND ANALYSIS

Sampling

Measurements presented in this report were made from the NASA Wallops Flight Facility Lockheed Electra. Flights over the North Atlantic Ocean were staged from Wallops Island, VA; flights over the South Atlantic Ocean were staged from Natal, Brazil.

Samples were drawn into the analytical systems through Teflon PFA tubing (1/4" OD for

DMS, 3/8" OD for H_2S) extending through bulkhead unions in the top of the aircraft. A 30 cm rearward facing rigid support ensured that samples were collected outside of the aircraft boundary layer. DMS samples or standards were drawn into the system using a small diaphragm pump while the aircraft was stationary, or a venturi pump while airborne. H_2S samples were collected only while airborne, using venturi pumps.

Dimethylsulfide Analysis

1. Oxidant Removal

All current methods for DMS analysis involve preconcentration based on either cryogenic condensation (Saltzman and Cooper, 1988; Maroulis and Bandy, 1977) or chemisorption (Braman *et al.*, 1978; Steudler and Kijowski, 1984; Andreae *et al.*, 1985) onto solid surfaces. The reactivity of DMS and the highly oxidizing nature of air has made the development of analytical techniques particularly challenging. The need for oxidant removal prior to preconcentration of DMS from air has been demonstrated in several studies (Ammons, 1980; Andreae *et al.*, 1985; Kuster *et al.*; 1986; Saltzman and Cooper, 1989; Goldan, 1990). These losses and conversions are generally attributed to the presence of ozone because sample losses (1) are associated with high levels of ozone in the sampled air, (2) can be simulated by the addition of ozone to gas streams, and (3) are alleviated by scrubbers which remove ozone from the sampled air. The actual mechanism of the interference is not known, but it is unlikely to result from the direct bimolecular reaction of ozone with DMS, which is relatively slow (Martinez and Herron, 1978). More likely the losses result from the production of highly reactive free radical species from the interactions of ozone with various surfaces. Oxidants other than ozone, particularly NO_x (NO + NO_2, may also be involved in sample loss.

The reaction of iodide (I^-) with ozone in neutral aqueous solution has been used for more than a century for the quantitative determination of atmospheric oxidants (Brodie, 1874). We have employed this reaction for sulfur gas analysis on the presumption that the product, triiodide ion (I_3^-), would be inert towards DMS. This indeed appears to be the case, as shown by a series of previously reported standard addition experiments (Saltzman and Cooper, 1989; Cooper and Saltzman, 1991).

The oxidant scrubbers used in this study were 250 ml glass bubblers with glass frits 20 mm in diameter. These contained 60 ml of neutral potassium iodide solution (2% w/v KI, 0.05 M KH_2PO_4 and 0.05 M Na_2HPO_4). Samples were drawn into the scrubbers through 1/4" OD Teflon PFA tubing, connected by Teflon TFE fittings (Cole Parmer Instrument Co., Chicago, IL). The scrubbers were mounted inside an insulated cooler in an ice/water mixture, lowering the water vapor content of the sample stream.

In normal use, the solution is routinely changed on a weekly basis, although no deterioration in performance has ever been noted. The theoretical capacity of this scrubber exceeds 1000 m^3 of air containing 100 ppbv of oxidants. By using an oxidant scrubber with such a large capacity, automated sampling and analysis of DMS and other reactive gases becomes possible. We have developed a system using Tenax GC (Alltech Associates, Inc., Chicago, IL) as a preconcentration medium for DMS, because of the relatively low temperatures required for desorption. The use of Tenax GC and other polymers for the determination of trace organics in air has previously been questioned due to the breakdown of the substrate and the release of various byproducts (Walling *et al.*, 1986). In the absence of an oxidant scrubber we have observed the conversion of DMS to dimethylsulfoxide and dimethylsulfone on Tenax columns, in addition to the appearance of elevated levels of organic components. The removal of oxidants from the sampled air stream was found to eliminate these interferences.

2. System Design and Operation

DMS and CS_2 are preconcentrated on Tenax GC cooled to approximately -20°C using a thermoelectric heat pump. These samples are desorbed thermally by reversing the voltage polarity to the thermoelectric units. Analysis is via gas chromatography using flame photometric detection.

A schematic diagram of the system is shown in Figure 1, and the timing cycle in Figure 2. The air stream is drawn first through the oxidant scrubber, then through a thermoelectrically cooled zone (TEC1 or TEC2), which contains a drier tube and Tenax trap. When sampling is complete, the sampling valve is switched and the polarity of the 12 VDC supply to TEC1 is reversed. This diverts the carrier gas through the Tenax trap and heats the block, desorbing the sample onto a cooled preconcentration column (TEC3). The air stream continues to flow through the now heated drier tube to waste, thus removing moisture which accumulated during sampling. After a brief transfer period, the polarity of the thermoelectric module cooling the preconcentration column is reversed, heating the unit and initiating the chromatographic run. Simultaneously with the injection of the sample collected on one channel, collection of the next sample on the second Tenax trap is started. After sample desorption, TEC1 or TEC2 is again cooled to begin the next sampling period. The total cycle time is 20 minutes per channel. Thus, with two channels operating alternately, one measurement is made every 10 minutes.

The system was calibrated manually during this study by switching of the air stream to sulfur-free air and injecting liquid standards (5-200 ul) onto a plug of silanized glass wool, Teflon wool, or directly into the KI bubblers. The preparation of liquid standards for CS_2 and DMS has been described previously (Saltzman and Cooper, 1988; Cooper and Saltzman, 1991). A typical calibration curve covers the range of 2-80 pmol, which is equivalent to 4-180 pptv in a 10 liter sample.

The thermoelectric units were clamped between an aluminum heat sink, mounted on the inside of an insulated cooler (0°C), and an aluminum block. For the two sampling channels, a 3/8" thick block was drilled to permit the entry of the drier tube and the Tenax sampling trap. The drier tube was 5/32" ID Teflon PFA tubing with no packing. The sampling trap was 1/4" ID Teflon PFA, packed with 35/60 mesh Tenax GC. All dead volume in the sampling tubes was packed with Teflon wool. A third 1/4" thick aluminum block was drilled to accept the preconcentration column, a 1/8" OD x 1/16" ID PFA tube packed with 60/80 or 35/60 mesh Tenax. This final focusing trap was needed in order to achieve a sharp injection of the analytes onto the chromatographic column.

The thermoelectric modules used in this study were obtained from TECA (model #950-127; Chicago, IL). These units are 1.6" x 1.6" x 0.15" in size and pump 51 watts at 12 VDC. With the heat sinks immersed in the ice bath, the temperature of the aluminum blocks during cooling was between -20 and -30°C. Stirring of the bath water with a submersible pump was necessary in order to attain these temperatures.

The sampling streams and carrier gas flows were routed through a 10 port, 1/8" gas injection valve (Valco Instruments Co., Inc., Houston, TX). The temperatures of the heated zones were controlled at 80°C using proportional controllers (model CN 9000, Omega Engineering; Stamford, CT). The thermoelectric units were operated at full load during cooling with no temperature control.

Air flow rates through the sampling channels were controlled using mass flow controllers (0-2 SLPM; MKS Instruments, Andover, MA) and the air volumes were integrated using a voltage-to-frequency converter and counter. The system was typically operated at air flow rates of 0.5 - 1.0 SLPM, with a sampling time of 10 minutes.

Chromatographic separation was achieved using a 1/8" x 8' Chromosil 330 column (Supelco Inc., State College, PA) held isothermal at 50°C. The carrier gas for the chromatographic separation was N_2 at 40 ml/min. These conditions provide baseline resolution between CS_2 and DMS. It should be noted that CS_2 emanates from many polymeric components in flow systems, and particular care is needed to ensure that the carrier gas stream is free from contamination. All tank gases used in the system were scrubbed with silica gel, molecular sieve, and charcoal prior to use. For the carrier gas and sulfur free air (for calibration) an additional Pd-coated molecular sieve trap (Science Glass, Miami, FL) was used immediately prior to the switching valve.

The sulfur gases were detected using a flame photometric detector (FPD, Tracor Instruments, Houston, TX) and a combined high voltage supply and electrometer (Pacific Instruments, Concord, CA). In order to minimize the effect of changes in cabin pressure on the detector response, the flame chamber was maintained at a constant pressure of 15 psia. The flame exhaust was flowed through an absolute back pressure regulator (Moore Products, Allentown, PA) to waste through a bulkhead in the airframe. This regulator was heated to 85°C to prevent condensation of water. The detection limit of the FPD is approximately 1 pmol of sulfur, which corresponds to 3 pptv of DMS or 1.5 pptv of CS_2 in a 10 liter sample. In practice, the system has a small CS_2 background, for which the samples are corrected. Because of the non-linear nature of the FPD, this has the effect of lowering the detection limit of CS_2 to less than 0.5 pptv.

The data acquisition and control functions were carried out using a PC-based chromatography software and A/D electronics package (OMS Tech, Miami, FL). This system provided timing and switching of valves and relays, real-time display and integration of the chromatogram, and storage of the chromatographic data and flow volumes to disk. The system was run on a laptop PC with an expansion chassis. An example of the real-time output from the system is shown in Figure 3.

3. Breakthrough Volumes for DMS Through Cooled Tenax Traps

The breakthrough characteristics of Tenax traps as a function of temperature were evaluated by operating the two sampling channels in series. Sequential air samples were analyzed on the second trap after passage through the first trap. The KI bubbler was spiked prior to starting each experiment using a DMS standard several times higher than a normal atmospheric sample. Flow rates of 0.1 - 0.5 liter/min air were used, with the normal sampling time of 10 minutes. For the purpose of this experiment, breakthrough was judged to occur when the first trace of DMS was evident in the second sample trap.

The temperature dependence of adsorption, and hence breakthrough, can be described using the Arrhenius relationship (Namiesnik, 1988). Results of the breakthrough experiments using DMS are shown in Figure 4 in the form of an Arrhenius plot. The relatively large scatter in the plot results from the fact that breakthrough volumes in this experiment could only be determined to $\pm$ 1 liter, and that temperatures generally drifted by $\pm$ 1°C during each run. This data can be used to predict the temperature requirement to achieve a given sample volume. A linear least squares fit of the data on a per gram Tenax basis gives the relationship $\log V/m = -9.897 + 3067/T$ ($r = 0.955$), where V is the maximum sampling volume in liters at an absolute temperature T. Using this relationship, a sampling volume of 10 liters on 0.21 g of Tenax requires a temperature of -8.2°C. By keeping the heat sinks of the thermoelectric units immersed in ice water, temperatures between -20 and -30°C are attained. This is sufficient to collect air samples of more than 30 liters before breakthrough occurs.

Hydrogen Sulfide Analysis

Hydrogen sulfide samples were collected and analyzed as described previously (Cooper, 1986; Saltzman and Cooper, 1988). Briefly, air was drawn through silver nitrate impregnated filters (47 mm, Whatman 41), after Natusch *et al.* (1972). Flow rates up to 16 l/min were used for sampling periods up to 110 minutes. Under these conditions the sensitivity of the method is less than 1 pptv. Flow rates were controlled manually using Teflon PFA needle valves (Cole Parmer, Chicago, IL), and monitored using mass flow meters (MKS Instruments, Inc). Sample volumes were obtained from totalizing the output signal of the mass flow meters. Samples were mostly collected as duplicate pairs of two filters in series. The sulfide signal on the back-up filter was used to correct for the interference of OCS on the front filter, in accordance with Cooper and Saltzman (1987). The value of this correction varied up to approximately 0.1 nmol per sample, equivalent to approximately 5 pptv sulfide in a typical sample.

The detection limit of the method and its precision at low concentrations is determined largely from the variability of the filter blanks. With only one exception (Flight 9) the blank variability within a given batch of filters was less than 20 pmol, equivalent to approximately 1 pptv on a single filter. This yields a precision of approximately 2 pptv in a 50 minute sample collected at 10 liter/min. These conditions represent the majority of the airborne intercomparison periods. A more practical estimate of the precision may be the relative standard deviation from the mean of duplicate samples, which averaged 24% in the 45 valid sample pairs.

The filters were stored in Teflon holders while on the aircraft, capped with Teflon plugs. Post-flight analysis was made by extracting the filters in 20 ml of 0.1M NaOH/NaCN, and measuring the fluorescence quenching of dilute fluorescein mercuric acetate with a Turner Designs fluorometer. Blanks were obtained from unexposed filters that were taken aboard the aircraft and treated identically to the samples.

RESULTS AND DISCUSSION

1. Overview

Results are presented here from the sixteen data missions flown during GTE/CITE-3. Flights 4-10 were conducted over the temperate North Atlantic from Wallops Island, VA, and flights 13-19 over the tropical South Atlantic from Natal, Brazil. The flight paths during the North Atlantic missions were chosen with the main objective of comparing the various instruments in the measurement of SO_2, DMS, OCS, H_2S and CS_2 over a wide range of concentrations. These paths are discussed in the project overview paper (Hoell *et al.*, 1992) and meteorological analysis (Shipham *et al.*, 1992). Air mass trajectory analyses show that North Atlantic tropical maritime air was sampled during most of flights 4 and 5. Continental air of Canadian polar origin was sampled during flights 6 and 9. Continental air from the northeast United States was sampled during flights 7,8 and 10.

The DMS and H_2S results obtained using the technique described in this report were in excellent agreement with the results of other investigators. No significant deviations were noted under any conditions encountered during the intercomparison study. Detailed descriptions of the intercomparison procedures and results are given by Gregory *et al.* (1992).

In addition to the airborne intercomparison, atmospheric and aqueous DMS was measured on board a research vessel by P.A. Matrai. This vessel was overflown twice during flights 6 and 7 to compare the atmospheric DMS measurements. Reasonable agreement was found, with airborne measurements of 11 - 30 pptv (mean 20.1, s=8.1, n=4) corresponding to shipboard measurements of 9 - 15 pptv (mean 12.6, s=3.0, n=3) during the two periods This simple test demonstates the lack of a near-surface gradient in atmospheric DMS under these meteorological conditions (wind speed 0 - 8 m/sec). This result is in contradiction to a similar experiment performed by Ferek and Bates (1989), possibly reflecting a more homogeneous DMS source during the present study. The greater variability in the aircraft data most likely results from the greater distance covered during each sample.

South Atlantic tropical maritime air masses were sampled during flights 13-19. Flight paths over the South Atlantic were selected primarily for the purpose of diurnal studies, with three pairs of duplicated missions. This paper focusses mainly on the spatial distribution of DMS, H_2S and CS_2 found during these flights, whilst the diurnal variation is discussed in more detail by Saltzman *et al.* (1992).

The boundary layer measurements of all compounds are summarized in Table 1, after grouping the data into the different air mass types discussed by Shipham *et al.* (1992). The highest average levels of DMS (median 124 pptv) occurred in marine air over the North Atlantic, the lowest levels in North American continental air (median 22 pptv). The highest levels of H_2S (median 57 pptv) were found in North American continental air, the lowest in South Atlantic marine air (median 2.5 pptv). Levels of CS_2 over the North Atlantic were similar in marine and continental air (median 5.8 and 4.2 pptv, respectively). In contrast, extremely low levels of CS_2 (median 0.7 pptv) were measured in South Atlantic marine air.

2. Distribution of Sulfur Compounds

2.1 North Atlantic

The boundary layer DMS concentrations are shown as a frequency distribution in Figure 5. A pronounced bimodal distribution is evident in the North Atlantic data, largely reflecting the difference between marine air and continental air. Most of the high DMS values (over 80 pptv) were measured in the tropical maritime air mass during flight 4 and the offshore leg of flight 5. During these legs the ozone concentrations were the lowest recorded in the North Atlantic flights, approximately 20 ppbv. High DMS levels (95-109 pptv) were also found in three samples during the inshore leg of flight 6. These data appear anomalous because the simultaneous measurements of ozone (approximately 50 ppbv) and carbon monoxide (approximately 180 ppbv) indicate a substantial degree of pollution. It appears from the trajectory analysis that the air flow was along the coast at this time, crossing productive coastal waters and extensive *Spartina* salt marshes. These environments have elevated emissions of reduced sulfur compounds relative to the open ocean (Cooper *et al.*, 1989; Cooper and Saltzman, 1991). An elevated H_2S concentration of 67 pptv was also measured at this time.

Maps of the North Atlantic DMS, CS_2 and H_2S data are shown in Figures 6 and 7. The high DMS levels in offshore areas correspond to the lowest levels of H_2S and CS_2. Conversely, the areas of high CS_2 and H_2S were generally low in DMS. This clearly demonstrates the influence of continental air masses on the speciation and concentrations of atmospheric sulfur gases present in the coastal air. The highest levels of H_2S and CS_2 were found off the New Jersey/New York coast, downwind of pollutant sources in the industrialized northeast U.S.

The DMS data over the North Atlantic Ocean are similar to previous shipboard studies (Andreae *et al.*, 1985; Cooper and Saltzman, 1991) and aircraft studies (Van Valin *et al.*; 1988). In a north-south transect off the east coast of the United States, Cooper and Saltzman (1991) found DMS concentrations reaching 120 pptv in easterly (onshore) air flow, dropping to less than 10 pptv in westerly (offshore) air flow. This range is almost identical to the present study. Van Valin *et al.* (1988) measured an average DMS level of 27 pptv close to the east coast of the U.S. and 54 pptv further offshore in the vicinity of Bermuda.

2.2 South Atlantic

The DMS concentrations from the South Atlantic boundary layer appear to have a bimodal distribution, similar to the North Atlantic data. However, there is no suggestion of advection over land masses in the five day back trajectories (Shipham *et al.*, 1992). Air at all but the highest aircraft altitudes was transported westward across the equatorial Atlantic during all flights. There is, however, evidence for the presence of haze layers or aged biomass burning plumes during some flights (Andreae *et al.*, 1992). This suggests that despite the seemingly homogeneous trajectories, there was variation in the source regions of air parcels at different altitudes. The highest level trajectories in some cases indicate recirculation from Brazil (most notably during flight 13), and in other cases indicate transport across the equator from northern Africa (most notably during flight 16). The highest DMS levels were measured during flight 17, reaching 82 pptv. During this flight the highest level trajectory showed transport across the equator from the Gulf of Guinea region.

There is also chemical evidence that the air encountered during the various boundary layer legs may have originated from different regions. This is demonstrated in the time series shown in Figure 8. With the exception of NO, all the species appear distinctly inhomogeneous. Carbon monoxide was significantly higher than average during most of flight 16, supporting the concept of air transport from the northern hemisphere. Flight 17 was characterized by high and homogeneous levels of both DMS and ozone, but significantly lower NO_y. The air mass sampled during this flight was clearly different from that sampled during flight 16, although the flights were made twelve hours apart over an identical path. During flights 14 and 15, also separated by twelve hours, the ozone and CO time series do not show significant changes. However, both CS_2 and NO_y decreased throughout the two flights, whereas DMS was higher during the second flight. This suggests that marine sources were progressively more dominant during this flight pair.

It is interesting to note that the DMS time series during flight 15 appears to show an inverse correlation with the NO_x levels. This raises the question of the possibility for nighttime removal of DMS by NO_3 in those parcels of air. However, the origin of these high NO_x levels is uncertain. In general they appear to coincide with spikes in total sulfur (Farwell *et al.*, 1992) and SO_2 (Thornton *et al.*, 1992) suggesting a pollution source, possibly due to plumes from ship traffic.

The relatively low DMS levels encountered over the South Atlantic (median 27 pptv) are somewhat surprising when compared to previous studies over tropical waters (Andreae and Raemdonck, 1983; Andreae *et al.*, 1985; Ferek *et al.*, 1986; Saltzman and Cooper, 1988). These levels suggest that the flux of DMS from the sea surface was smaller than encountered previously. This is not surprising in view of the facts that (1) the air mass trajectories indicate transport over the central South Atlantic gyre, which is a relatively unproductive water mass, and (2) this study was conducted at the end of austral winter, which corresponds to the seasonal minimum in phytoplankton growth.

The average boundary layer H_2S and CS_2 concentrations were significantly lower over the South Atlantic than the North Atlantic. The H_2S and CS_2 levels measured in South Atlantic marine air during this study (median 2.5 and 0.7 pptv, respectively) are the lowest values available in the published literature. All previous studies have been conducted in the northern hemisphere (Maroulis and Bandy, 1980; Kim and Andreae, 1987; Cooper and Saltzman, 1991).

The South Atlantic data are mapped in Figure 9. Unlike the North Atlantic data, there are no clear geographic gradients in the DMS levels, even though significant variability is evident in the boundary layer data. An interesting feature evident in the maps of the South Atlantic DMS data is the occurrence of relatively high DMS levels in several of the samples taken at 5000 ft, which were considered to be free tropospheric air. This suggests that a portion of the sample was enriched in air from the boundary layer. Two explanations for such an enrichment are (1) that boundary layer air had been transported vertically through cloud processes, as proposed by Chatfield and Crutzen (1983) and noted previously by Ferek *et al.* (1986) or (2) that the height of the boundary layer depth was close to 5000 ft, so that boundary layer air was collected for at least part of the sample. The simultaneous dew point and ozone profiles also show abrupt changes at about 6000 ft altitude.

In general, there does not appear to be any significant change in the depth of the trade wind inversion layer between any of the seven South Atlantic flights, although significant structure was sometimes observed within this inversion (Saltzman *et al.*, 1992; Shipham *et al.*, 1992). However, the occurrence of high DMS levels in the boundary layer did not coincide with changes in this structure, ruling out the possibility that the DMS variability was a direct result of mixing height changes.

3. Diurnal Variation in Atmospheric DMS, CS_2 and H_2S

Day/night flight pairs were conducted over the South Atlantic for the purpose of studying diurnal variability. The map of the DMS distribution (Figure 9) shows that considerable variation was occurring between flights over identical paths. The ratio of nighttime maximum to daytime minimum found between flights 16 and 17, a factor of approximately three, is considerably higher than found previously in remote marine air (Andreae *et al.*, 1985; Berresheim, 1987; Cooper and Saltzman, 1988). A nighttime/daytime ratio of approximately 1.5 was found during flights 14 and 15, similar to the previous studies. Flights 18 and 19 were conducted sequentially on the same day, with sunrise occurring in the middle of flight 18. In this case the DMS declines steadily in a manner that is consistent with fairly rapid daytime photochemical removal.

While the large difference in DMS levels between flights 16 and 17 appear to be due to a slightly different air mass trajectory, the air mass trajectories and the tracers shown in Figure 8 suggest that the conditions during flights 18 and 19 were similar. The rapid decrease in DMS during this flight pair therefore suggests that either (1) oxidant levels may have been higher than previously encountered in remote marine air or (2) vertical mixing processes may have intensified during the flights. These differences have been discussed in detail by Saltzman *et al.* (1992).

Diurnal variation by a factor of approximately 2 in H_2S levels is also consistent with the preceding discussion. The diurnal variation of CS_2, though smaller, appears to support a change in source between flights 16 and 17, with the highest levels occurring during the daytime flights. This suggests that variation in the sources of these compounds produced the observed temporal variability in the first two flight pairs, and not oxidation processes.

4. Vertical Profiles of DMS, CS_2 and H_2S

The free tropospheric measurements of DMS, H_2S, and CS_2 are summarized in Table 2. It is clear that DMS and H_2S concentrations were significantly lower in the free troposphere than the boundary layer (Table 1), which is consistent with a sea surface source for these compounds. In contrast, levels of CS_2 in the free troposphere were not significantly different to those in the boundary layer. This suggests that horizontal advection may be an important source of CS_2 to the marine atmosphere. The lifetime of CS_2 to oxidation by OH is approximately four times longer than DMS or H_2S (Hynes and Wine, 1990). This allows the presence of CS_2 in aged continental air over the oceans, in which much of the continental H_2S has already been oxidized. This effect may also explain the similarity between CS_2 levels in the North Atlantic marine and continental air masses (Table 1). Even though the marine air has reached steady state with oceanic DMS, it may still contain residual pollutants from its previous landfall. Long range transport of pollution from Europe has been observed under similar circumstances in aerosol data taken at Barbados (Savoie *et al.*, 1989).

In order to study the vertical gradient of the reduced sulfur gases in more detail, the data from all flights have been averaged into groupings containing measurements made in narrow altitude ranges (approximately 1000 ft intervals). Although not strictly vertical profiles due to the large geographic distances covered and the use of data from multiple flights, the composite profiles represent the range of values at a given altitude within the range of the study. The composite vertical profiles of DMS and CS_2 obtained using this averaging procedure are shown in Figures 10 and 11. There is no significant difference between the North Atlantic and the South Atlantic DMS profiles, but the greater standard deviation of the northern hemispheric data reflects the inclusion of both marine and continental air masses. The DMS data are similar to previously published vertical profiles (Ferek *et al.*, 1986; Andreae *et al.*, 1988), and are clearly consistent with a sea surface DMS source. Small, but measurable levels of DMS (up to 3 pptv) were found up to 17000 ft.

In contrast, both the North Atlantic and South Atlantic CS_2 profiles show a maximum above the boundary layer. This confirms the possibility of advective processes carrying continental CS_2 long distances over the oceans, which may constitute a greater source of CS_2 to the marine atmosphere than emissions from the sea surface.

Composite vertical profiles of H_2S are shown in Figure 12. In this case, the individual data points are plotted with no averaging. The data show similar structure to the DMS vertical profiles, with the only major difference being the extremely low H_2S levels in the South Atlantic. Although the South Atlantic H_2S data are sparse, there is a hint of a maximum corresponding to the CS_2 maximum at an altitude of 10,000 - 14,000 ft. This would be consistent with a continental origin of free tropospheric H_2S in addition to an oceanic source.

5. Implications for the Global Sulfur Cycle

Although the highest DMS levels were found in the North Atlantic tropical maritime air, the ratio of DMS to H_2S and/or CS_2 in this air mass was similar to the ratio evident in both the South Atlantic marine air and the previous study of Saltzman and Cooper (1988). Table 3 shows the relative contribution of the various reduced sulfur species to non-sea-salt sulfate, based on these concentrations and the most reliable oxidation rate measurements. Clearly DMS accounts for the majority of the background sulfate in all the marine air masses. The relative contribution of these gases to non-sea-salt sulfate in continental air is likely to be variable, depending on the history of the air mass. The reduced sulfur gas levels measured in continental air during this study would account for an insignificant fraction of non-sea-salt sulfate when compared to the high levels of sulfur dioxide measured simultaneously by other investigators

(Thornton *et al.*, 1992), which are presumably anthropogenic.

The average levels of H_2S and CS_2 found in the North Atlantic tropical maritime air masses (mean 8.4 and 6.4 pptv, respectively) are similar to those reported by Saltzman and Cooper (1988) and Kim and Andreae (1987), respectively. The average levels measured in the southern hemisphere (median 2.5 and 0.7 pptv) are significantly lower than in the previous studies. The H_2S levels are approximately a factor of three lower than found in the North Atlantic tropical maritime air masses, and the CS_2 levels almost an order of magnitude smaller. These low levels further constrain the importance of biogenic emissions of these compounds in global budgets. The evidence for advection of air from the continents to the remote marine free troposphere suggests that oceanic sources of these compounds may also be smaller than previously assumed from atmospheric concentrations.

A potential implication of the extremely low background levels of CS_2 found in the South Atlantic boundary layer is that continental (presumably anthropogenic) sources may have been underestimated previously. The oxidation of CS_2 leads to formation of OCS, which may be important in controlling the background stratospheric sulfate aerosol (Crutzen, 1976). More study is required to quantify the global OCS budget.

Acknowledgements. This work was supported by NASA grant NAG1918 and NSF grant ATM 87-09802. Thanks are due to the expert technical assistance of David Odum of OMS Tech (Miami, FL) and Tom Snowdon of the University of Miami.

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Table 1. Summary of all boundary layer sulfur gas measurements. Concentration units are pptv.

	North Atlantic		South Atlantic
	Marine	Continental	Marine
Dimethylsulfide			
Median	124.1	22.2	26.7
Mean	118.0	27.2	34.0
Sigma (n)	13.3 (11)	18.8 (77)	16.8 (97)
Hydrogen Sulfide			
Median	n/a	57.0	2.5
Mean	8.4	116.8	2.9
Sigma (n)	1.2 (2)	138.7 (14)	1.4 (13)
Carbon Disulfide			
Median	5.8	4.2	0.7
Mean	6.4	5.4	0.9
Sigma (n)	1.3 (11)	4.8 (77)	0.7 (97)

Table 2. Summary of all free tropospheric sulfur gas measurements. Concentration units are pptv.

	North Atlantic		South Atlantic
	Marine	Continental	Marine
Dimethylsulfide			
Median	11.7	4.7	4.7
Mean	12.4	5.3	6.8
Sigma (n)	7.6 (15)	3.3 (39)	6.9 (58)
Hydrogen Sulfide			
Median	2.3	17.6	1.0
Mean	3.0	20.5	1.0
Sigma (n)	3.2 (4)	14.7 (6)	2.2 (9)
Carbon Disulfide			
Median	2.3	2.3	0.4
Mean	4.2	6.7	0.8
Sigma (n)	4.8 (15)	8.0 (43)	1.0 (58)

Table 3. The relative contribution (%) of various sulfur containing species to background (non-sea-salt) sulfate. Rate constant units are cm^3 $molecule^{-1}$ sec^{-1}, taken from Hynes *et al.* (1986), Barnes *et al.* (1986), Hynes and Wine (1989), and Wahner and Ravishankara (1989) for 298K and 760 Torr.

Species	Rate Constant	North Atlantic Marine	North Atlantic Continental	South Atlantic Marine
DMS	6.0×10^{-12}	93.8	30.8	91.5
H_2S	5.0×10^{-12}	5.3	68.1	7.2
CS_2	1.1×10^{-12}	0.8	0.9	0.4
OCS	2.0×10^{-15}	0.1	0.2	0.5

FIGURE CAPTIONS

Fig. 1. Schematic of the automated DMS/CS_2 analytical system. Reversing temperature zones are indicated by the shaded boxes. Gas flow is indicated by solid lines, electrical connections are indicated by dashed lines.

Fig. 2. Schematic of the sampling cycle used during CITE-3. Shaded areas correspond to active periods, blank areas correspond to inactive periods.

Fig. 3. A typical chromatogram, taken in the boundary layer during flight 15. The concentrations measured were 54 pptv DMS and 0.7 pptv CS_2. The internal standard was generated by injecting a small (less than 50 ul) loop of a gaseous DMS standard after the initial sample injection. It is equivalent to 9 pptv in this sample.

Fig. 4. Results of experiments to determine the breakthrough volume of DMS through Tenax GC as a function of temperature.

Fig. 5. Frequency distribution of the DMS measurements made during GTE/CITE-3.

Fig. 6a. Maps of DMS data over the North Atlantic Ocean. The east coast of the U.S. is shown from Georgia to Massachussetts. The upper plot shows the free tropospheric data, the lower plot shows the boundary layer data. Note the different scales on the vertical axes.

Fig. 6b. Maps of CS_2 data over the North Atlantic Ocean. The east coast of the U.S. is shown from Georgia to Massachussetts. The upper plot shows the free tropospheric data, the lower plot shows the boundary layer data.

Fig. 7. Maps of H_2S data over the North Atlantic Ocean. The upper plot shows the free tropospheric data, the lower plot shows the boundary layer data. The east coast of the U.S. is shown from South Carolina to New Jersey. Boxes are plotted to show the geographic range of each sample. Note the different scales on the vertical axes.

Fig. 8. Line graph showing all boundary layer DMS and CS_2 measurements with the corresponding 10 minute averaged measurements of ozone, carbon monoxide, NO_x and NO_y.

Fig. 9a. Maps of DMS data over the South Atlantic Ocean. The upper plot shows the free tropospheric data, the lower plot shows the boundary layer data. Note the different scales on the vertical axes.

Fig. 9b. Maps of CS_2 data over the South Atlantic Ocean. The upper plot shows the free tropospheric data, the lower plot shows the boundary layer data.

Fig. 10. Vertical profiles of DMS measured over (A) the North Atlantic and (B) the South Atlantic. All data from constant altitude legs are included. The symbols represent the means of the data at various altitudes, with the standard deviation shown as horizontal bars.

Fig. 11. Vertical profiles of CS_2 measured over (A) the North Atlantic and (B) the South Atlantic. All data from constant altitude legs are included. The symbols represent the means of the data at various altitudes, with the standard deviation shown as horizontal bars.

Fig. 12. Vertical profiles of H_2S measured over (A) the North Atlantic and (B) the South Atlantic. All data from constant altitude legs in all flights are included.

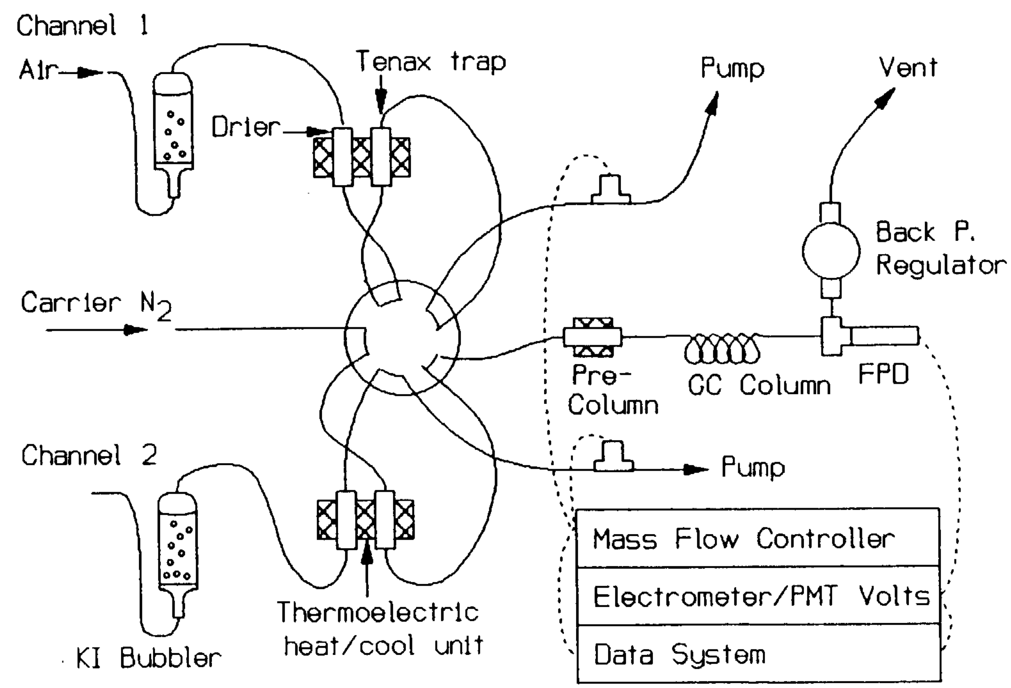

Channel 1
Air
Drier
Tenax trap
Pump
Vent
Back P. Regulator
Carrier N_2
Pre-Column
GC Column
FPD
Pump
Channel 2
KI Bubbler
Thermoelectric heat/cool unit
Mass Flow Controller
Electrometer/PMT Volts
Data System

Fig 2

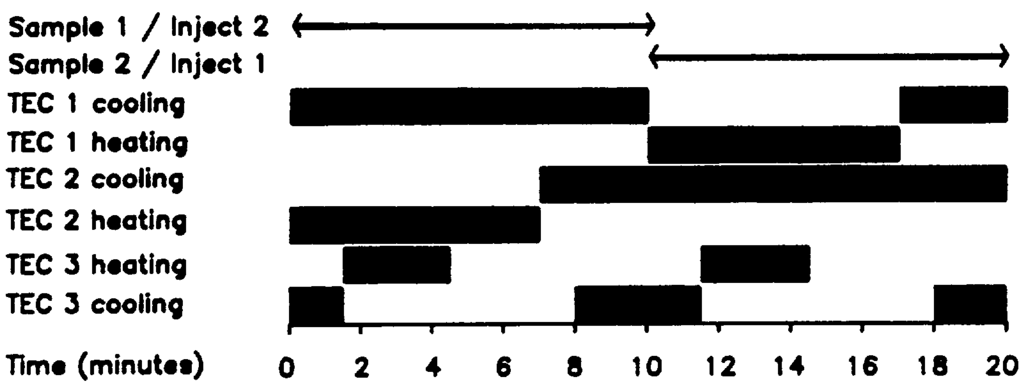
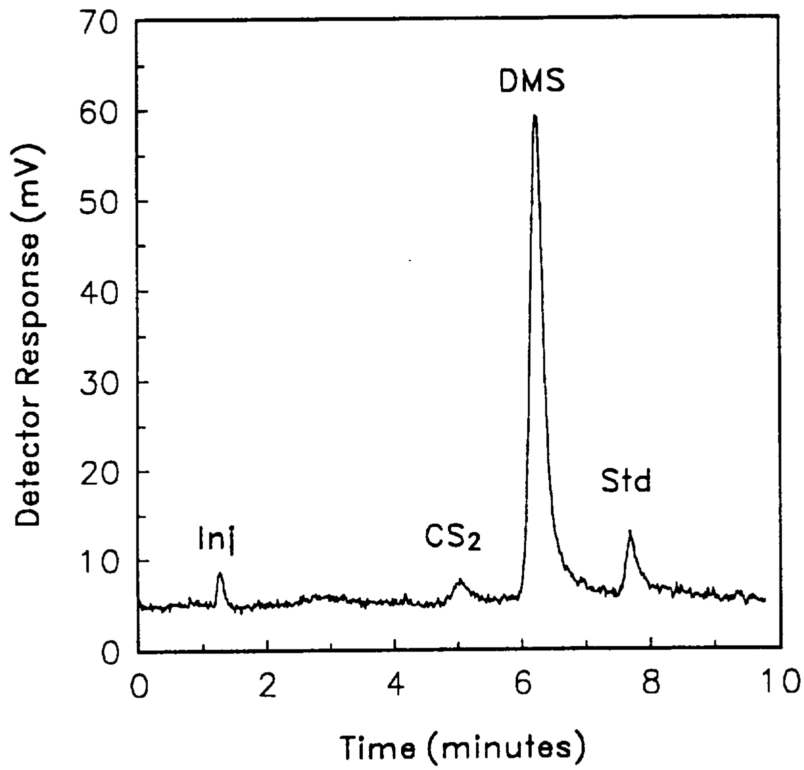
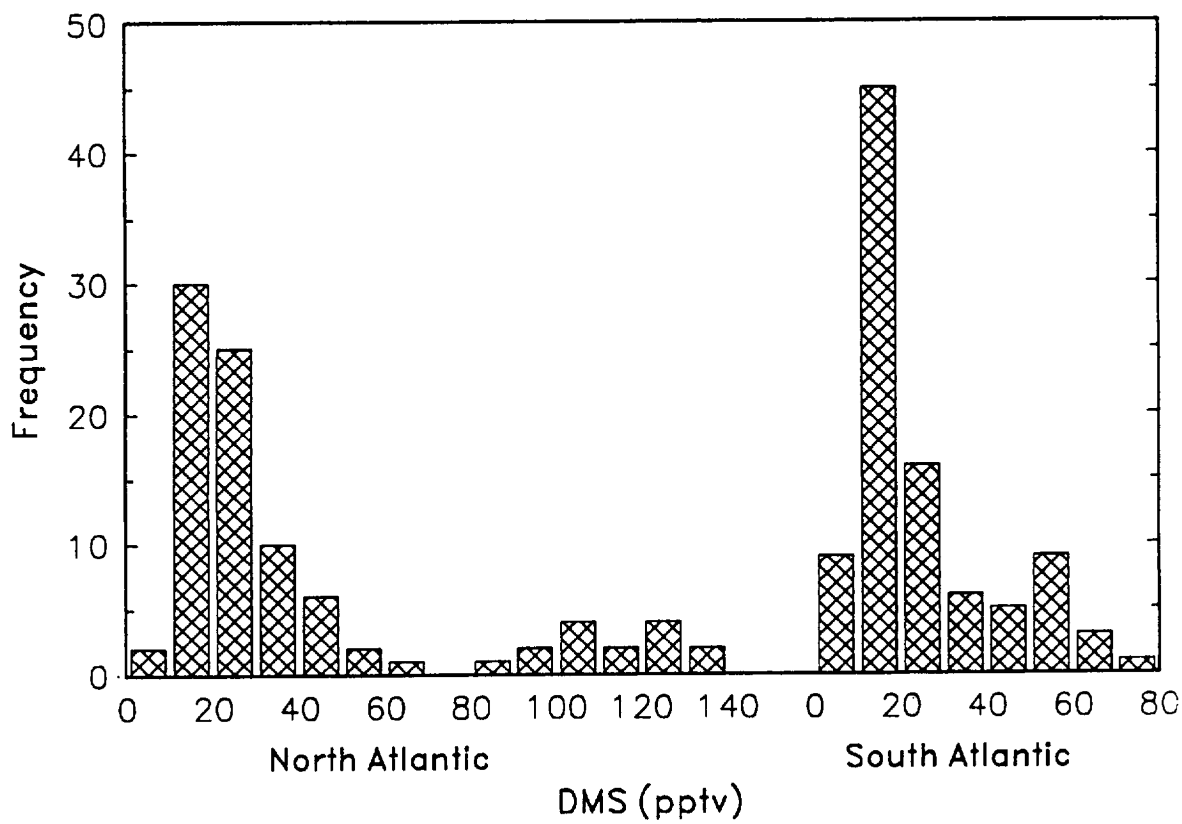

Sample 1 / Inject 2
Sample 2 / Inject 1
TEC 1 cooling
TEC 1 heating
TEC 2 cooling
TEC 2 heating
TEC 3 heating
TEC 3 cooling
Time (minutes)
0
2
4
6
8
10
12
14
16
18
20

Fig 3



DMS
Std
Inj
CS_2
Detector Response (mV)
Time (minutes)
70
60
50
40
30
20
10
0
0
2
4
6
8
10

Fig 5



Frequency
50
40
30
20
10
0
0
20
40
60
80
100
120
140
0
20
40
60
80
North Atlantic
South Atlantic
DMS (pptv)

Fig 6a

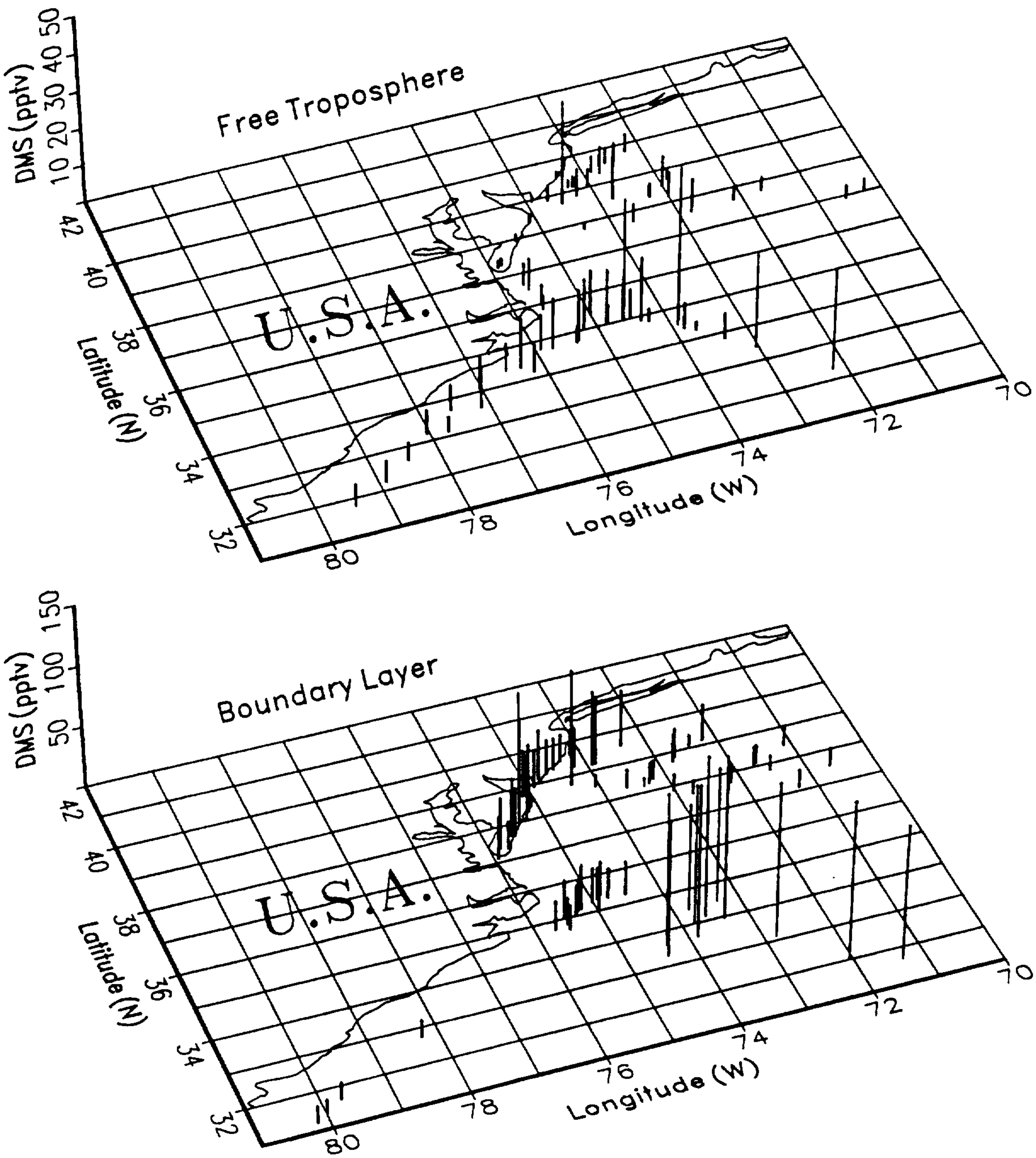
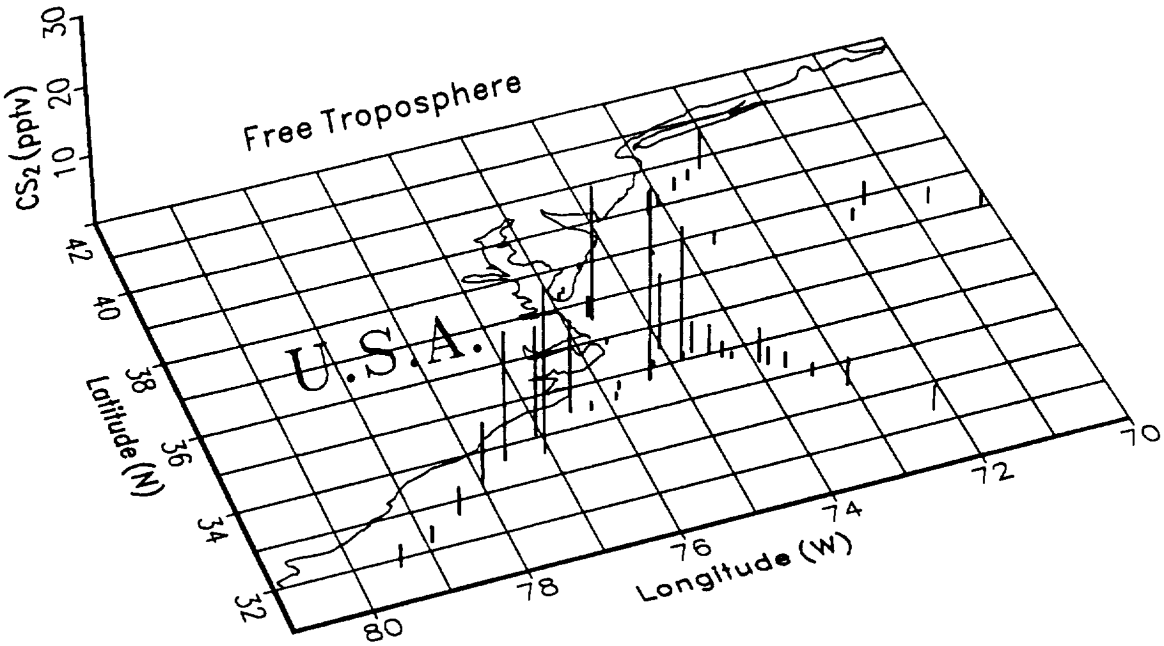
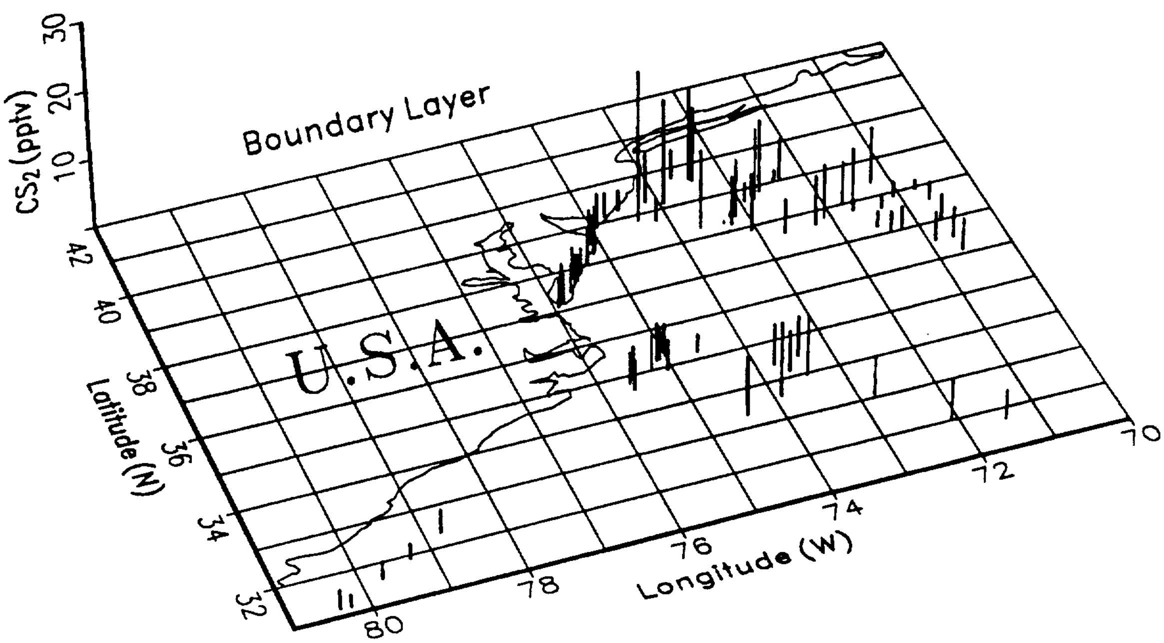

Free Troposphere
DMS (pptv)
10 20 30 40 50
U.S.A.
Latitude (N)
42 40 38 36 34 32
Longitude (W)
80 78 76 74 72 70
Boundary Layer
DMS (pptv)
50 100 150
U.S.A.
Latitude (N)
42 40 38 36 34 32
Longitude (W)
80 78 76 74 72 70

Fig 6b

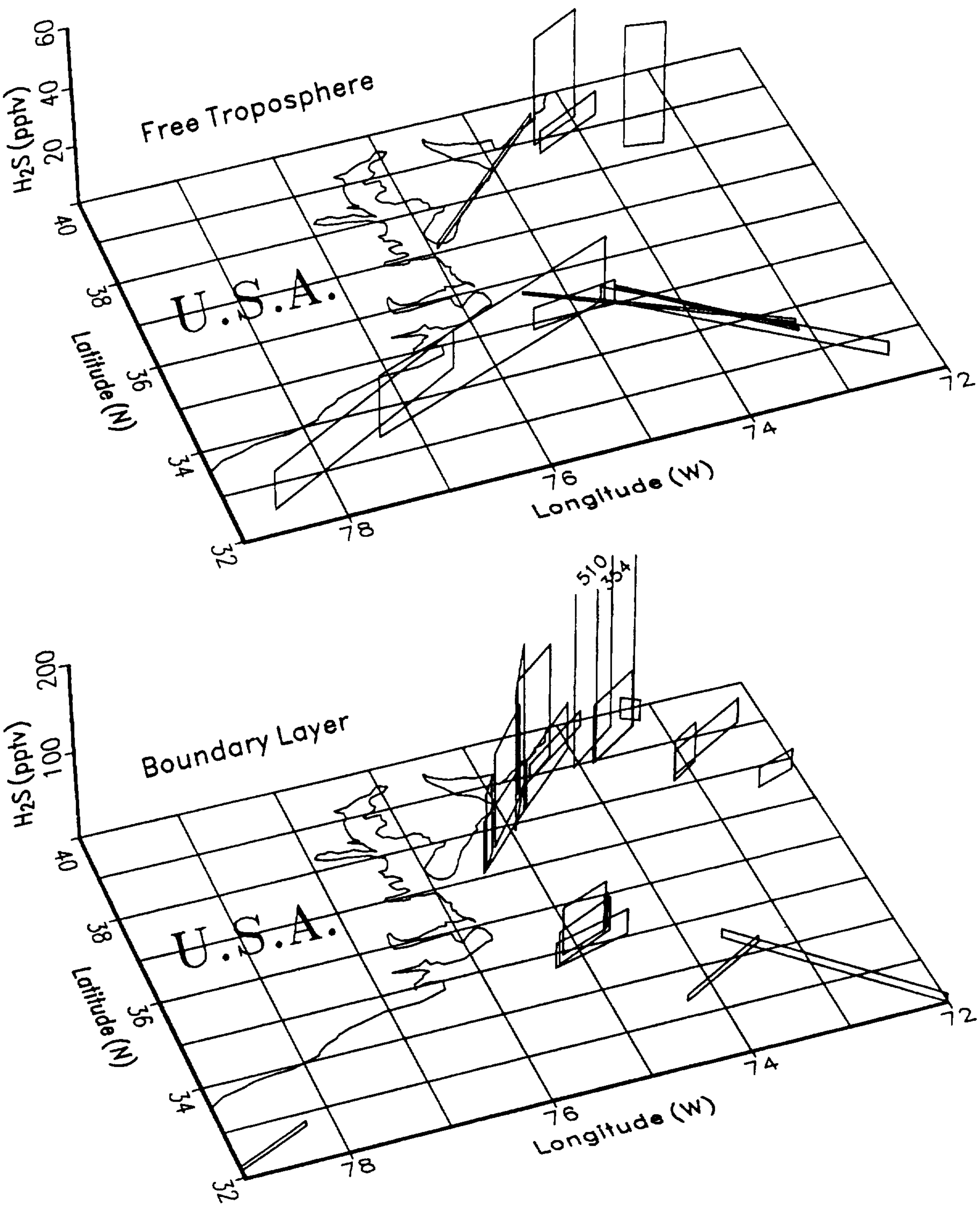


Free Troposphere
CS_2 (pptv)
30
20
10
42
40
38
36
34
32
Latitude (N)
U.S.A.
80
78
76
74
72
70
Longitude (W)



Boundary Layer
CS_2 (pptv)
30
20
10
42
40
38
36
34
32
Latitude (N)
U.S.A.
80
78
76
74
72
70
Longitude (W)

Fig 7


Free Troposphere
H2S (pptv)
60
40
20
40
38
36
34
32
Latitude (N)
U.S.A.
78
76
74
72
Longitude (W)
Boundary Layer
H2S (pptv)
200
100
510
354
40
38
36
34
32
Latitude (N)
U.S.A.
78
76
74
72
Longitude (W)

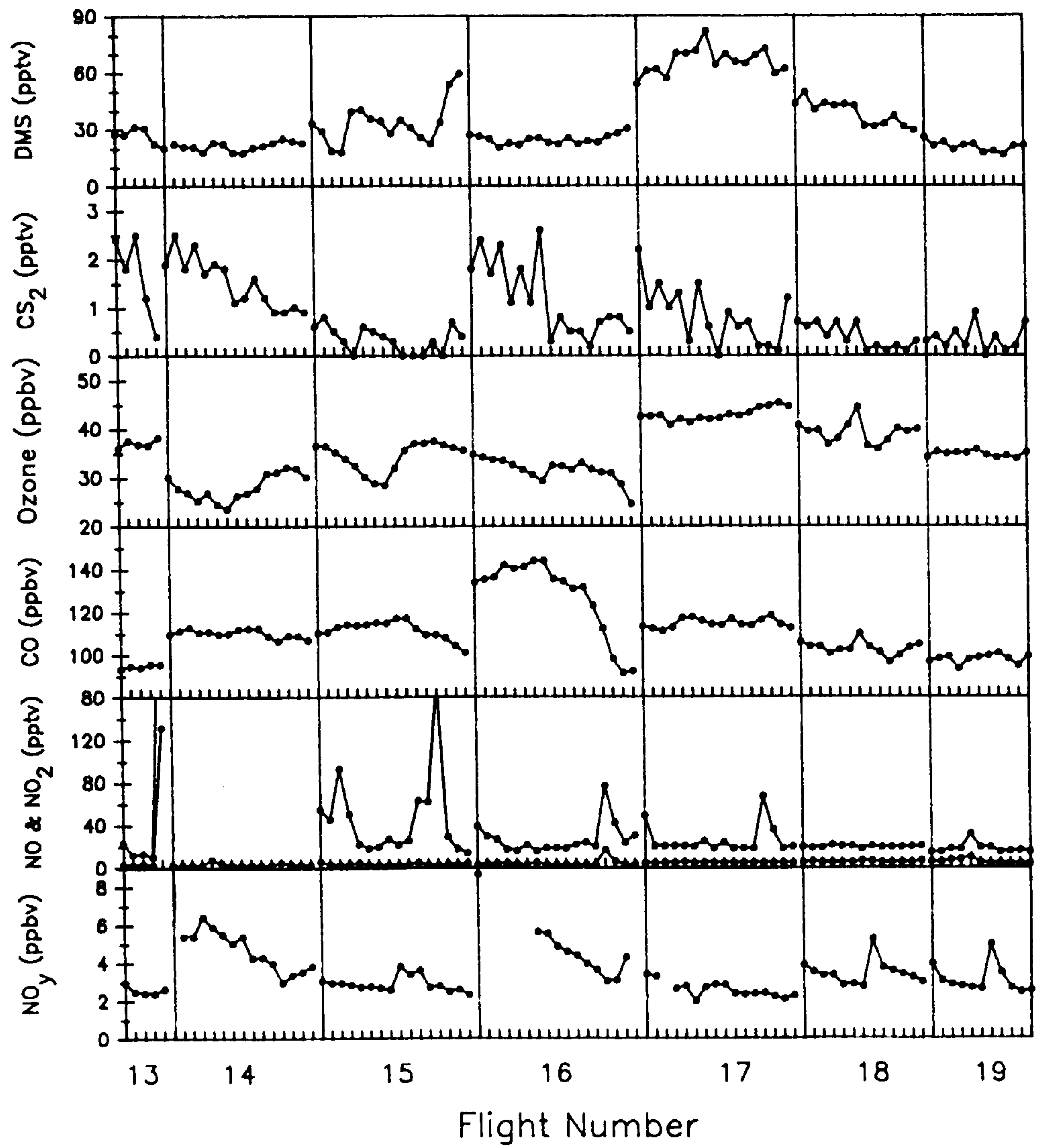
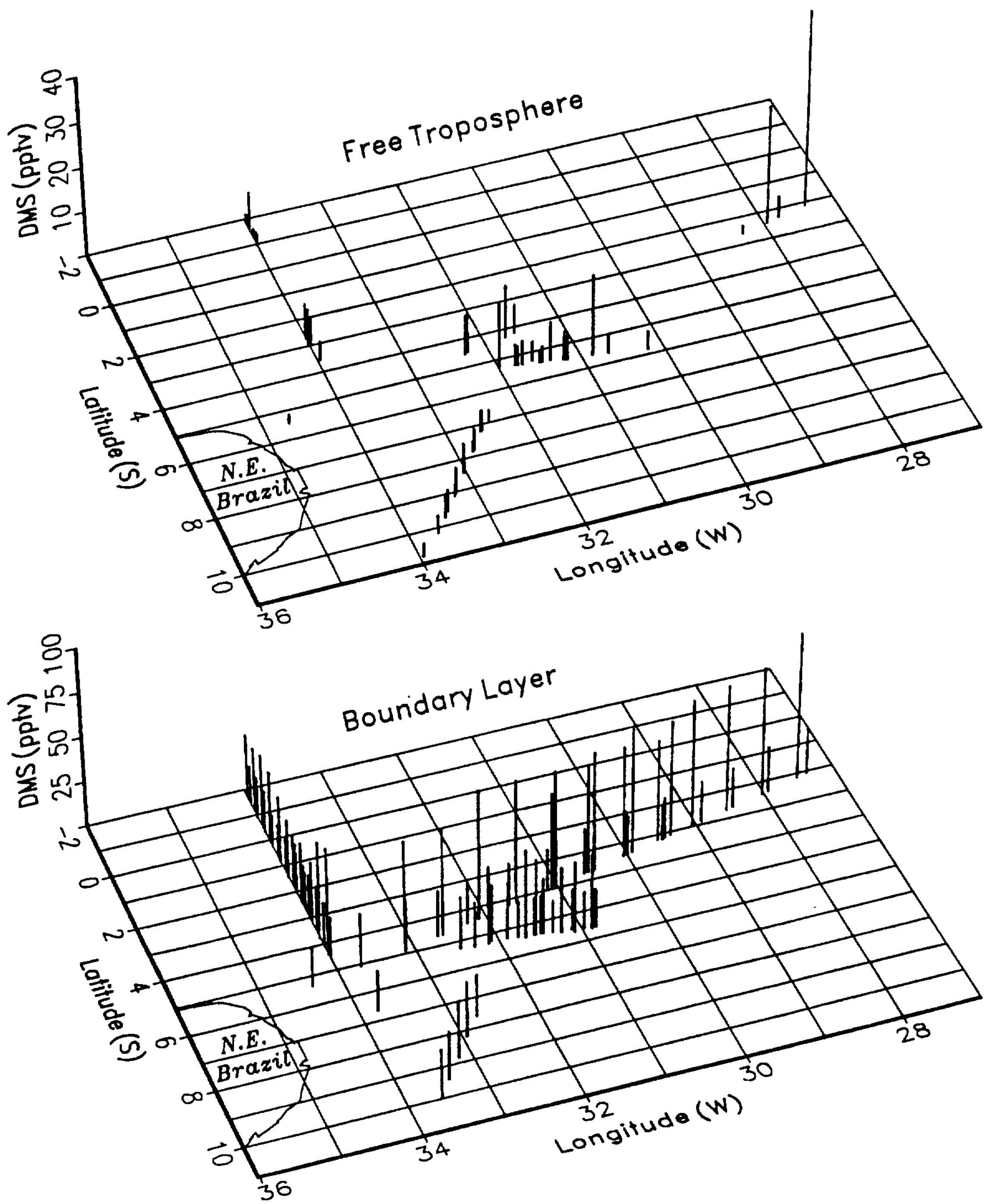
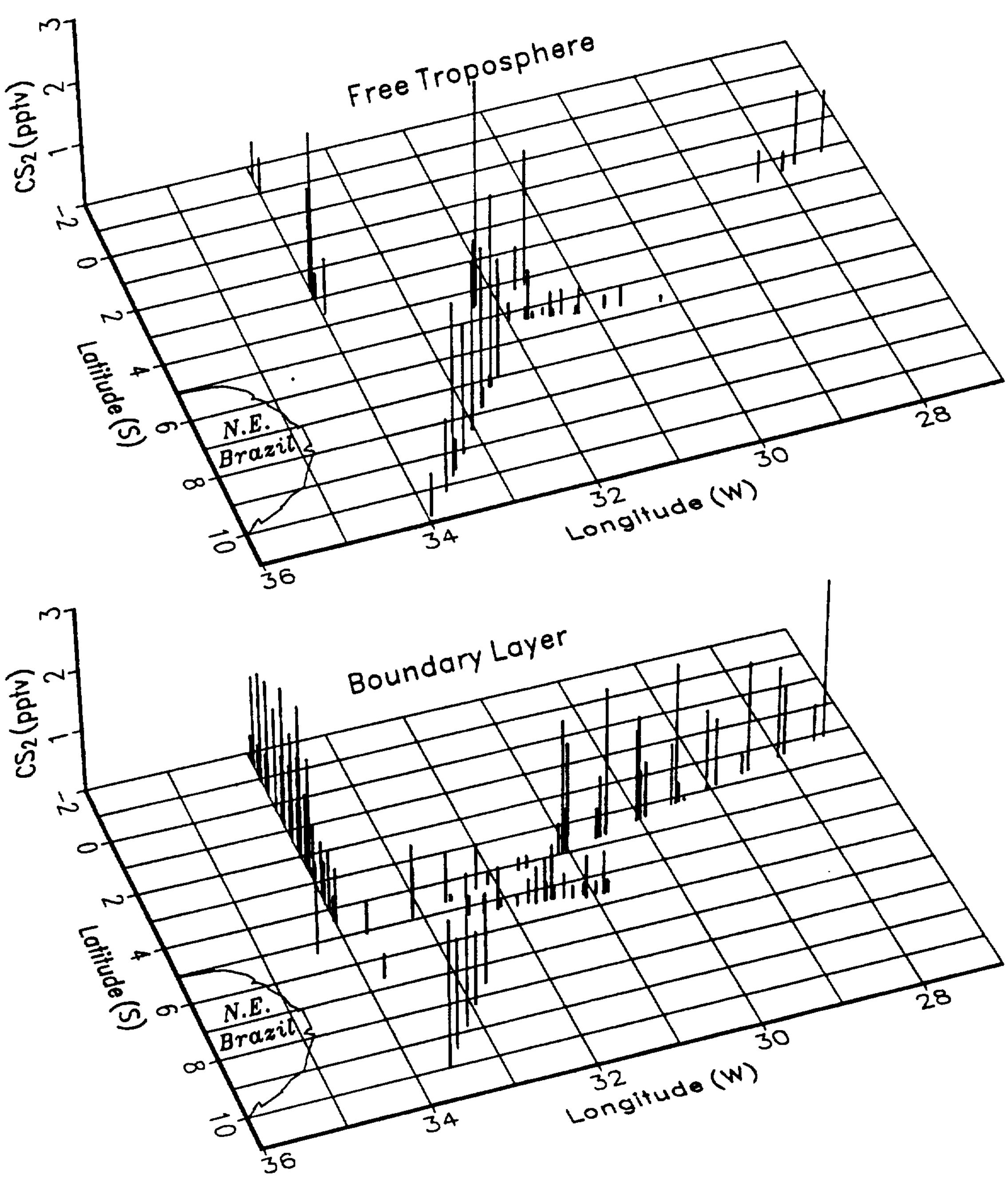

DMS (pptv)
CS2 (pptv)
Ozone (ppbv)
CO (ppbv)
NO & NO2 (pptv)
NOy (ppbv)
90
60
30
0
3
2
1
0
50
40
30
20
140
120
100
80
120
80
40
0
8
6
4
2
0
13
14
15
16
17
18
19
Flight Number

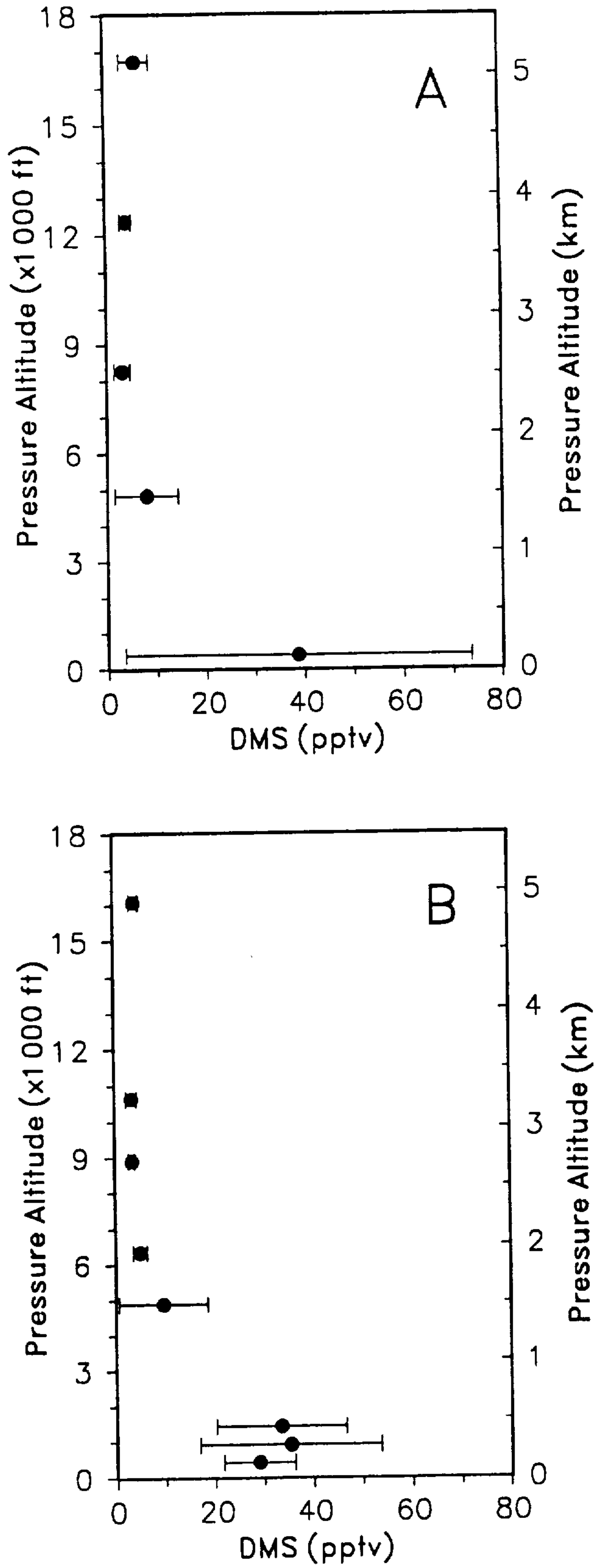
Fig 9a



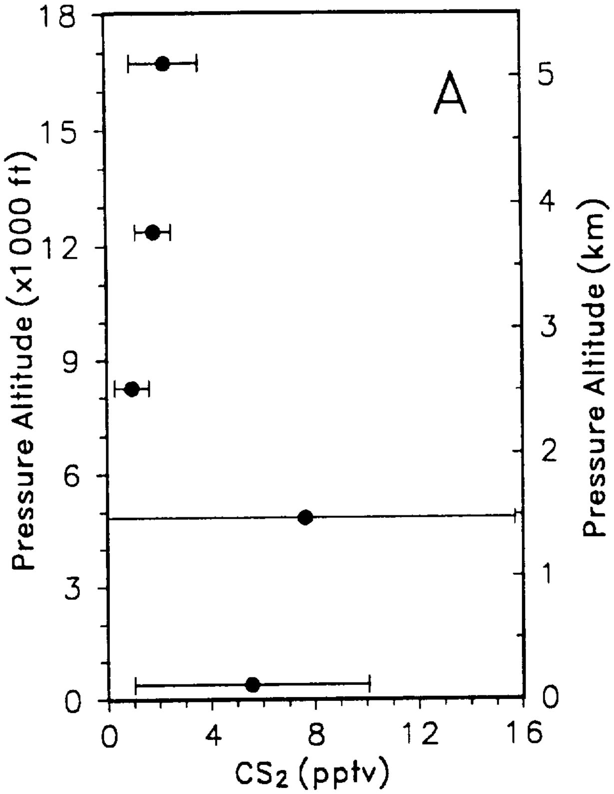
Free Troposphere
DMS (pptv)
40
30
20
10
-2
0
2
4
6
8
10
Latitude (S)
N.E.
Brazil
36
34
32
30
28
Longitude (W)
Boundary Layer
DMS (pptv)
100
75
50
25
-2
0
2
4
6
8
10
Latitude (S)
N.E.
Brazil
36
34
32
30
28
Longitude (W)

Fig 9b


Free Troposphere
CS_2 (pptv)
3
2
1
-2
0
2
4
6
8
10
Latitude (S)
N.E.
Brazil
36
34
32
30
28
Longitude (W)
Boundary Layer
CS_2 (pptv)
3
2
1
-2
0
2
4
6
8
10
Latitude (S)
N.E.
Brazil
36
34
32
30
28
Longitude (W)


A
Pressure Altitude (x1 000 ft)
Pressure Altitude (km)
DMS (pptv)
0
3
6
9
12
15
18
0
1
2
3
4
5
0
20
40
60
80
B
Pressure Altitude (x1 000 ft)
Pressure Altitude (km)
DMS (pptv)
0
3
6
9
12
15
18
0
1
2
3
4
5
0
20
40
60
80

Fig


A
Pressure Altitude (x1 000 ft)
Pressure Altitude (km)
CS2 (pptv)
18
15
12
9
6
3
0
5
4
3
2
1
0
0
4
8
12
16

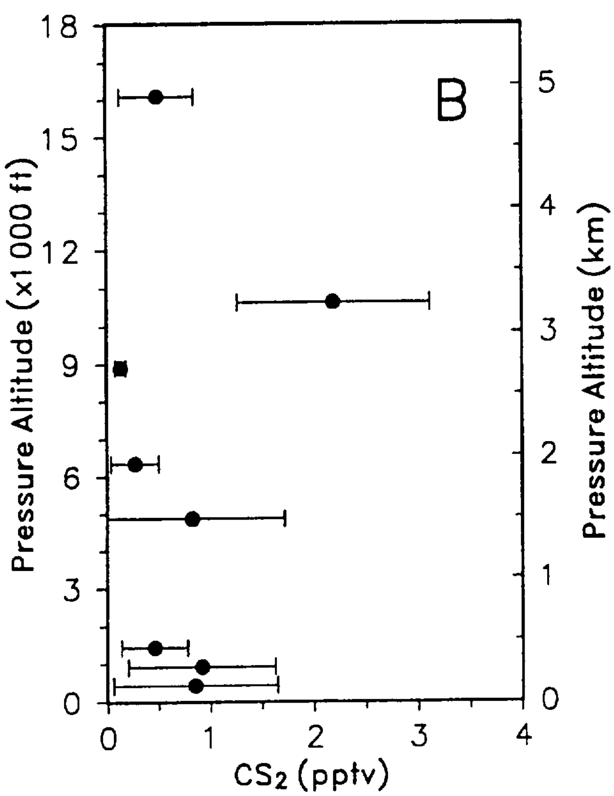
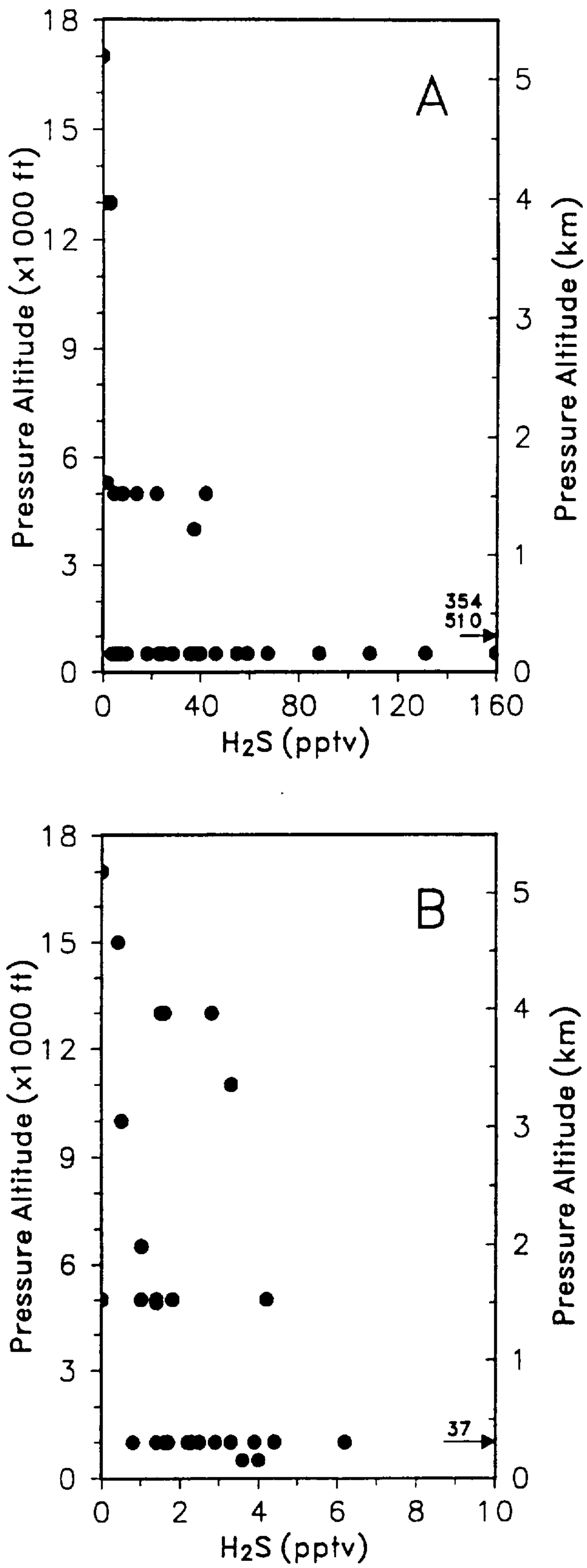

B
Pressure Altitude (x1 000 ft)
Pressure Altitude (km)
CS2 (pptv)
18
15
12
9
6
3
0
5
4
3
2
1
0
0
1
2
3
4

Fig 12.


A
Pressure Altitude (x1 000 ft)
Pressure Altitude (km)
H2S (pptv)
354
510
B
Pressure Altitude (x1 000 ft)
Pressure Altitude (km)
H2S (pptv)
37